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C08G 18/48**(21) Application number: **96112666.1**(22) Date of application: **08/06/1996**(84) Cited Signatory States:  
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2018 Antwerp (BE)(30) Priority: **08/18/1995: DE 19530388**(71) Applicant: **BAYER AG**  
**51368 Leverkusen (DE)****(54) Purified polyether polyols, a process for their manufacture, and their use.**

(57) Higher molecular weight polyether polyols having little odor are obtained by distilling the polyether polyols that are to be purified while adding 5 to 30% water, by weight, at temperatures of 110 to 150°C and at pressures of 10 to 70 hPa, such that the water is led through the polyether polyols in a dosage time of 1 to 5 hours in finely dispersed form with a drop diameter of 5-100 µ.

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**Specification**

The present invention pertains to higher molecular weight polyether polyols having little odor, a process for their manufacture, as well as their use for the manufacture of polymers, cosmetics, and pharmaceutical products. that are built upon polyether polyols.

In the technical manufacture of polyether polyols by the alkoxylation of suitable starter compounds with Zerewitinoff-active hydrogen atoms, after the reaction mixture is neutralized, after the dehydration and subsequent filtration of inorganic salts, polyether polyols, which contain, depending upon the processing method, 0.1 to 2% residual water by weight, up to 2% solvent by weight (generally an organic solvent), and substances that impart an odor, such as aldehydes, dioxolanes, dioxanes, allyl alcohol, as well as mono-, di- and tripropylene glycolallyl ethers. Even though these substances, which impart an odor, are generally present in no more than small quantities, they do, however impart a characteristic, intensive, aromatic odor to the polyether polyols.

In technology, therefore, various methods of purification have been developed and described for the purpose of removing from the polyether polyols the undesired by-products, which result from their manufacture. Thus, for example, in DE-A2 755 089, an improved process for the removal of disturbing by-products, especially small quantities of water and solvent as well as low molecular weight glycols and intensively odoriferous substances by means of a serpentine tube evaporator is described. What is disadvantageous about this process, however, is the fact that the organic solvents that are present are removed only incompletely, and the aforementioned intensively odoriferous substances are removed to no more than a slight degree. An additional disadvantage of the process described in the aforementioned German revealed patent application is the high expenditures in terms of apparatus that are associated with it.

In principle, folded film evaporators can be used for the purification of the polyether polyols as well. However, they exhibit the same disadvantages as the purification process by means of a serpentine tube evaporator that was described in the aforementioned revealed patent application.

In the Japanese patent application 56/104 936, a method for the purification of polyether polyols is described in which at a pH of  $> 6.5$ , either the crude polyether polyols are distilled under decreased pressure at high temperature, or in which water, water vapor, or nitrogen, also at decreased pressure and elevated temperature, is led through the crude polyether polyols. As comparison example 2 of the aforementioned Japanese patent application shows, however, when water is conducted through the crude polyether-polyol mixture, the disturbing odor-imparting substances are removed to just an inadequate degree. The corresponding analytical values and odor samples show this. In addition, the polyether polyols that were obtained according to comparison example 2 were less stable, that is, the aldehyde content in the polyether polyols increased, as did the unpleasant smell.

Thus, it was now the task of the present invention to make polyether polyols available whose odor-forming by-products were, removed in the greatest measure, which are, therefore, practically odor-free. Such practically odor-free polyether polyols thus meet today's standards, particularly when they are used to produce polyurethanes and soft polyurethane foams, which are used, in turn, in the manufacture of furniture or mattresses. In addition, high standards of purity are imposed in the cosmetic industry and in the pharmaceutical industry upon the polyether polyols that are used in them, standards which the polyether polyols according to the invention can meet.

Therefore, mono-functional and polyfunctional polyether polyols that have little odor are the object of the present invention, polyols whose molecular weight is 750 to 18000, preferably 1000 to 15000, most especially preferably 2000 to 12000 (calculated on the basis of OH number and functionality:

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$$\text{Mol. Wght.} = \frac{\text{FOH} \times 56 \times 100}{\text{OH number}}$$

and whose viscosity, determined at 25°C with a Höppler viscosimeter according to DIN<sup>1</sup> 53015, is 40 to 25000, preferably 50 to 10000 mPa • s, which are characterized by the fact that their content in terms of the following, amounts to:

- a) 2-methyl-2-pentenal < 1.5 ppm, preferably < 0.2 ppm,
- b) allyl alcohol < 1.0 ppm, preferably < 0.2 ppm,
- c) allyloxypropanol < 15 ppm, preferably < 5.0 ppm,
- d) dipropylene glycol allyl ether < 50 ppm, preferably < 0.5 ppm,
- e) propionaldehyde < 1.0 ppm, preferably < 0.2 ppm.

It is well known that the polyether polyols that are claimed according to the invention are produced by the polymerization of epoxides, such as ethylene oxide, propylene oxide, butylene oxide, tetrahydrofurane, styrene oxide, or epichlorohydrin with themselves, for example, in the presence of acids, or by the addition of these epoxides, if necessary, in the mixture or one after another, in the presence of acids or preferably, of strong bases as catalysts, to starter components with reactive hydrogen atoms. Examples of such starter components are n-butanol, n-hexanol, phenol, water, ethylene glycol, 1,2 and 1,3-propylene glycol, 1,4-butane diol; 4,4'-dihydroxy-diphenyl propane, glycerine, trimethylolpropane, erythritol, sorbitol, ammonia, ethylene diamine, aniline, ethanol amine, and triethanol amine. In addition, sucrose polyethers, as described, for example, in the German document laid open to public inspection 1 176 358 and in 1 064 938, and polyethers that have been modified by vinyl polymers, as they occur, for example, as a result of the polymerization of styrene and acrylonitrile in the presence of polyethers (US 3 383 351, 3 304 273, 3 523 093, 3 110 695, DE-B 1 152 536), can be purified according to the invention. Polyether polyols on a basis of ethylene oxide and/or propylene oxide with 1 to 8, preferably 2 to 6 hydroxyl groups, whose molecular weights and viscosities lie in the range indicated above, are preferred.

A further object of the present invention is a process for the production of higher molecular weight polyether polyols having little odor, that is characterized by the fact that the polyether polyols that are to be purified are distilled while adding 5.0 to 30.0 % water by weight, preferably 7.0 to 25.0%, relative to the polyether polyols that are used, at temperatures of 110 to 150°C, preferably 115 to 140°C, and at a pressure of 10 to 70 hPa, preferably 20 to 50 hPa, such that the water is conducted through the polyether polyols in a dosing period of 1 hour to 5 hours, preferably 2 to 4 hours, in finely dispersed form having a drop diameter of 5.0 to 100 µ, preferably 7 to 50 µ.

It is important for the process according to the invention that during the distillation of the polyether polyols that are to undergo purification that the water be added in such doses that the lower temperature limit not be undercut during distillation and that the upper pressure limit not be exceeded.. This is brought about, in particular by means of the prescribed dosage time of the water that is added in finely dispersed form to the polyether polyols that are to be purified. If the prescribed conditions of distillation are not adhered to, odor-forming substances in the polyether polyols are removed to no more than an insufficient degree.

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<sup>1</sup>German Industrial Norm—Trans.

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As has been mentioned before, it is likewise of significance for the process according to the invention that the water be introduced to the polyether polyols in the form of very small drops. This can be accomplished, for example, by means of a capillary tube, a fine ceramic frit, a sintered metallic frit, or by means of fine pressurized jets or pneumatic dual substance jets.

A thorough mixing of the distillation mixture is indicated so that the water that is introduced makes intensive contact with the polyether polyols that are to be purified. The well known mixing devices, such as cross-beam mixers, coarse screen mixers, or ultra thorax mixers can be used for this purpose.

The process according to the invention can follow the well known polyether polyol production methods as a separate purification step. It is understood that it is also possible to subject commercially available polyether polyols to subsequent purification using the process according to the invention in order to obtain the commercially available polyether polyols in a practically odor-free form.

The polyether polyols according to the invention, which have little odor, can be used for the manufacture of low-emission polymers that are built upon a basis of polyether polyols, such as polyurethanes, especially soft polyurethane foams, elastomers, or for the manufacture of cosmetics and pharmaceutical products.

**Examples**

In the examples that follow, 1000 g of the most varied polyether polyols were heated to 120°C. At a pressure of 18 hPa, 200 g of water (20% by weight) were introduced via thin introduction pipes (2 mm in diameter) at such a velocity that the temperature of 120°C was not undercut and the pressure did not increase in excess of 40 hPa. The dosage time for the water that was added was 3 hours. The water bubbles had a mean diameter of 7 to 50  $\mu$ . Di- and tri-functional PO and PO/EO polyethers were used in the examples. From Table 1 it is possible to see the effect of the distillation according to the invention upon the impurities in the polyether polyols that were used. It may be seen clearly that after distillation according to the invention, the undesired by-products, which lead, among other things, to the formation of an odor, were removed to the greatest degree. The analysis took place by means of headspace gas chromatography.

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Table 1

Compounds in the polyether polyols	Example 1		Example 2	
	before distillation	after distillation	before distillation	after distillation
1,4-dioxane	<0.1	<0.1	<0.1	<0.1
2,4 dimethyl-1,3-dioxalane	1.5	<0.1	<0.1	<0.1
2-ethylene-4-methyl-1,3-dioxolone	2.5	<0.1	<0.1	<0.1
2-methyl-2-pentenal	1.8	<0.1	2.2	<0.1
Acetaldehyde	1.2	0.1	1.9	2
Allyl alcohol	<0.1	<0.1	0.6	<0.1
Allyloxy-propanol	80	<0.1	0.6	<0.1
Butyraldehyde	<0.1	<0.1	<0.1	<0.1
DPG Allyl ether	460	<0.1	480	<0.1
Propionaldehyde	1.1	0.1	0.4	0.3
Total of unknown readily volatile compounds	20	8	15	8
Compounds in the polyether polyols	Example 3		Example 4	
	before distillation	after distillation	before distillation	after distillation
1,4-dioxane	<0.1	<0.1	<0.1	<0.1
2,4 dimethyl-1,3-dioxalane	<0.1	<0.1	<0.1	<0.1
2-ethylene-4-methyl-1,3-dioxolone	1.2	<0.1	<0.1	<0.1
2-methyl-2-pentenal	6	0.3	0.3	<0.1
Acetaldehyde	0.5	0.8	0.6	1.3
Allyl alcohol	1.8	<0.1	<0.1	<0.1
Allyloxy-propanol	170	1.4	12	0.3
Butyraldehyde	<0.1	<0.1	<0.1	<0.1
DPG Allyl ether	650	<0.1	55	<0.1
Propionaldehyde	2.7	0.1	0.3	0.3
Total of unknown readily volatile compounds	8	8	8	4
All indications in ppm				

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The polyether in Example 1 was a branched polyether on a basis of glycerine, ethylene oxide and propylene oxide, OHN 46 (OH Number) Molecular weight (Mw): 3660, viscosity: 560 mPa • s.

The polyether in Example 2 was a linear polyether on a basis of propylene glycol and PO, OHN 112, Mw: 1000, viscosity 140 mPa • s.

The polyether in Example 3 was a linear polyether on a basis of propylene glycol and PO, OHN 56, Mw: 2000, viscosity 310 mPa • s.

The polyether in Example [sic-4?] was a branched polyether on a basis of trimethylol propane, PO and EO, OHN 28. Mw: 6000, viscosity: 1120 mPa • s.

EO = Ethylene oxide, PO = propylene oxide

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## Patent Claims

1. Mono-functional and poly-functional polyether polyols having little odor, whose molecular weight lies at 750 to 18000, preferably at 1000 to 15000, particularly preferably at 2000 to 12000 (calculated by OH number and functionality)

$$\text{Mol. Wght.} = \frac{\text{FOH} \times 56 \times 100}{\text{OH number}}$$

and whose viscosity, at 25°C, determined with a Höppler viscosimeter according to DIN<sup>2</sup> 53015, is 40 to 25000, preferably 50 to 10000 mPa • s, which are characterized by the fact that their content, in terms of the following amounts to:

- a) 2-methyl-2-pentenal, < 1.5 ppm, preferably < 0.2 ppm,
  - b) allyl alcohol, < 1.0 ppm, preferably < 0.2 ppm,
  - c) allyloxypropanol, < 15 ppm, preferably < 5.0 ppm,
  - d) dipropylene glycol allyl ether, < 50 ppm, preferably < 0.5 ppm,
  - e) propionaldehyde, < 1.0 ppm, preferably < 0.2 ppm.
2. A process for the manufacture of polyether polyols according to claim 1, characterized by the fact that the polyether polyols that are to be purified are distilled at temperatures of 110 to 150°C and at pressures of 10 to 70 hPa, with the addition of 5 to 30% water by weight, relative to the polyether polyols that are used, such that the water is led, in finely dispersed form, through the polyether polyols to be purified, in a dosage period of 1 to 5 hours, with a drop diameter of 5 to 100 µ.
  3. The use of the polyether polyols according to claim 1, which have little odor, for the manufacture of low-emission polymers, cosmetics, and pharmaceutical products, which are built upon polyether polyols.

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<sup>2</sup>German Industrial Norm-Trans.